

**EFFECT OF SOLVENTS AND TEMPERATURES ON PHOTO-REDUCTION  
OF CARBON DIOXIDE USING ALUMINA DOPED  $\text{TiO}_2$  CATALYSTS**

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## **ABSTRACT**

Photo-reduction is the most promising method to reduce carbon dioxide to a valuable product such as methanol. Apart of a simple process, photo-reduction also has a great potential to become a method for renewable energy in the future. In this study, the effects of solvents and temperatures in photo-reduction of CO<sub>2</sub> were examined. The sol-gel method used for Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalysts preparation was also reported. The result shows for both solvents which are H<sub>2</sub>O and NaOH were able to react with CO<sub>2</sub> to concentration methanol. Somehow, solubility of CO<sub>2</sub> in NaOH is rather higher than H<sub>2</sub>O to concentration the methanol. The result analysed shown that the concentration of methanol in both NaOH and H<sub>2</sub>O were increasing with time. Somehow, the application of NaOH as solvent has shown better result compared to H<sub>2</sub>O where the concentration of methanol in NaOH was always greater than H<sub>2</sub>O for every time elapsed. The highest concentration of methanol in NaOH was 63 ng/μL while 43 ng/μL in H<sub>2</sub>O. Meanwhile, the effectiveness of temperatures shown the highest concentration of methanol was found at T= 60 °C. Since the boiling point of methanol is 65 °C, the production of methanol was limited. The liquid phase of methanol has changed to vapour phase which leads to the concentration of methanol was maximized within the ranges of temperatures as analyzed.

# **KESAN PELARUT DAN SUHU PADA FOTO REDUKSI KARBON DIOKSIDA MENGUNAKAN KATALIS ALUMINA DIDOPKAN $\text{TiO}_2$**

## **ABSTRAK**

Foto-reduksi adalah cara yang paling menjanjikan untuk menukarkan karbon dioksida menjadi produk yang berharga seperti metanol. Selain dari proses yang mudah, foto-reduksi juga memiliki potensi besar untuk menjadi sebuah cara untuk pembaharuan tenaga pada masa hadapan. Dalam kajian ini, pengaruh pelarut dan suhu dalam foto-reduksi  $\text{CO}_2$  telah diperiksa. Cara sol-gel digunakan untuk penyediaan  $\text{Al}_2\text{O}_3\text{-TiO}_2$  katalis juga dilaporkan. Hasilnya menunjukkan untuk kedua-dua pelarut iaitu  $\text{H}_2\text{O}$  dan  $\text{NaOH}$  mampu bertindak balas dengan  $\text{CO}_2$  untuk menghasilkan metanol. Walau bagaimanapun, kelarutan  $\text{CO}_2$  di  $\text{NaOH}$  agak lebih tinggi berbanding  $\text{H}_2\text{O}$  untuk menghasilkan metanol. Hasilnya dianalisis menunjukkan bahawa kepekatan metanol dalam kedua-dua  $\text{NaOH}$  dan  $\text{H}_2\text{O}$  meningkat dengan masa. Namun, apabila  $\text{NaOH}$  digunakan sebagai pelarut telah menunjukkan hasil yang lebih baik berbanding  $\text{H}_2\text{O}$  dimana kepekatan metanol dalam  $\text{NaOH}$  adalah sentiasa lebih besar berbanding  $\text{H}_2\text{O}$  untuk setiap masa berlalu. Kepekatan tertinggi metanol dalam  $\text{NaOH}$  ialah  $63 \text{ ng} / \mu\text{L}$  manakala  $43 \text{ ng} / \mu\text{L}$  dalam  $\text{H}_2\text{O}$ . Sementara itu, keberkesanan suhu telah menunjukkan hasil tertinggi metanol didapati di  $T = 60^\circ\text{C}$ . Takat didih metanol ialah  $65^\circ\text{C}$ , maka penghasilan metanol menjadi terhad. Fasa cecair metanol telah berubah menjadi fasa wap yang membawa kepada hasil metanol telah dimaksimumkan dalam julat suhu sebagaimana di analisa.

## TABLE OF CONTENTS

<b>TITLE PAGE</b>	<b>i</b>
<b>SUPERVISOR DECLARATION</b>	<b>ii</b>
<b>STUDENT DECLARATION</b>	<b>iii</b>
<b>ACKNOWLEDGEMENT</b>	<b>v</b>
<b>ABSTRACT</b>	<b>vi</b>
<b>ABSTRAK</b>	<b>vii</b>
<b>LIST OF TABLES</b>	<b>x</b>
<b>LIST OF FIGURES</b>	<b>xi</b>
<b>CHAPTER 1 INTRODUCTION</b>	
1.0 Research Background	1
1.1 Problem Statement	3
1.2 Research Objectives	4
1.3 Scopes of Study	4
1.4 Organization of the Thesis	5
<b>CHAPTER 2 LITERATURE REVIEW</b>	
2.0 Introduction to Carbon Dioxide	7
2.1 Photo-Reduction of CO <sub>2</sub>	8
2.2 Efficiency of CO <sub>2</sub>	9
2.3 Significance of CO <sub>2</sub> Recycling For Methanol Production	10
2.4 Introduction to Catalyst	11
2.4.1 Alumina (Al <sub>2</sub> O <sub>3</sub> )	11
2.4.2 Titanium Dioxide (TiO <sub>2</sub> )	12
2.4.3 Mechanism of titanium dioxide (TiO <sub>2</sub> )	14
2.5 Effect of Solvents	15
2.5.1 H <sub>2</sub> O as Solvent	16
2.5.2 NaOH as Solvent	17
2.6 Effect of Temperatures	18

2.7	Chronology of Methanol Production	19
2.8	Alternative Method to Produce Methanol As Fuel	21
2.9	concentration of Methanol	22
2.10	High Performance Liquid Chromatography (HPLC)	23
2.11	Mobile Phase Selection	25

### **CHAPTER 3 MATERIALS AND METHODS**

3.0	Introduction	27
3.1	Chemical and Materials	27
3.2	Preparation of Catalyst by Sol-Gel Method	28
3.3	Photo-Reduction of CO <sub>2</sub>	30
	3.3.1 Effect of Solvents	30
	3.3.2 Effect of Reaction Temperature	31
3.4	Analyzing Methanol by Using HPLC	31

### **CHAPTER 4 RESULTS AND DISCUSSION**

4.1	Introduction	33
4.2	Effects of Solvents	34
4.3	Effect of Reaction Temperatures	36

### **CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS**

5.1	Conclusions	39
5.2	Recommendations	40

<b>REFERENCES</b>	41
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<b>APPENDICES</b>	43
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## LIST OF TABLES

TABLE	TITLE	
PAGE		
B.1	Concentration of Methanol in Comparison Solvent	45
B.2	Concentration of Methanol by Variation of Temperatures	45

## LIST OF FIGURES

FIGURE PAGE	TITLE	
1.1	Mechanism of Photo-reduction	14
3.1	Preparation of $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$ Catalyst	29
3.2	Flow chart of overall experiment works	32
4.1	Effect of Solvent in Photo-Reduction of $\text{CO}_2$	34
4.2	Effect of Temperatures in Photo-reduction of $\text{CO}_2$ with NaOH	37
A.1	Standard Curve for Methanol Yield	44

## **CHAPTER ONE**

### **INTRODUCTION**

#### **1.0 Research Background**

Carbon dioxide (CO<sub>2</sub>) is the most significant component for greenhouse gas produced by human activities. The main source of CO<sub>2</sub> production is the combustion of fossil fuels. Since the Industrial Revolution, the concentration of CO<sub>2</sub> has risen by more than 30 percent and grows up till now. One of the effects of excess CO<sub>2</sub> formation is global warming which lead to raise the sea level and melt the ice at the North Pole. The concentration of CO<sub>2</sub> in the atmosphere also becomes a toxic gas to human body. The effects to human are headache, sweating, restlessness, short of breath, increased heart beat and blood pressure and visual distortion (Robert and John, 1960).

It is important to treat the excess of CO<sub>2</sub> to be a useful product. Therefore, photocatalytic reduction is the best method to achieve that purpose. According to this method,



CO<sub>2</sub> was transform to methanol by the presence of catalyst. In this study, Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> catalyst was used in photo-catalytic reduction process assisted by UV light.

Photo-catalytic reduction process is the acceleration of a photoreaction in the presence of a catalyst. Photo-catalytic reduction of CO<sub>2</sub> process is used UV light as energy to break the CO<sub>2</sub> bonds and lead to the production of methanol. Al<sub>2</sub>O<sub>3</sub> catalyst is widely used in different industrial chemical processes such as hydrodesulphurization, dehydration and cracking. As transition alumina has higher surface area and chemical activity, it has been used extensively as a catalyst or catalyst support because of the excellent properties such as high surface area, good catalytic activity, good mechanical strength, high hardness, and transparency. Generally, Wang et. al., (2005) stated that the stabilization of alumina can be promoted by doping it with foreign elements such as alkaline-earth metals, rare-earth metals and silicon. In this study, metal alumina was doped with TiO<sub>2</sub> as a heterogeneous catalyst in photo-reduction process to produce methanol as a valuable product.

Methanol is widely used in various fields. It is not only for heating purpose, but also important to form goods. About 40 % of methanol is converted to formaldehydes diverse as plastics, plywood, paints, explosives, and permanent press textiles. Another application of methanol is used as a solvent and antifreeze in pipelines and windshield washer fluid. In some wastewater treatment plants, a small amount of methanol is added to wastewater to provide a carbon food source for the denitrifying bacteria, which convert nitrates to nitrogen to reduce the nitrification of sensitive aquifers (Valerie et. al., 2003).

Methanol has a long history of use in racing vehicles where it is valued both its power producing properties and its safety aspects where methanol is harder to ignite, creates less radiant heat and burns without producing black smoke. Methanol use in non-racing vehicles has been much less successful. There was significant interest in using methanol as a gasoline blending component for its octane value and emissions. Several methanol or co-solvent blends were approved for use but the oxygenate methyl tertiary butyl ether which used methanol in its manufacture was preferred (Richard et. al., 2007).

The concentration of CO<sub>2</sub> in atmosphere seems need to be reduced as maximum as we can so that the global warming phenomena can be reduced to the minimum level. The photo-catalysis reduction of CO<sub>2</sub> to methanol contributes a lot of benefit to the world. This study was focused on two types of solvents which were NaOH and H<sub>2</sub>O to find the best solvent in photo-catalytic reduction process. Effect of reaction temperature in photo-catalytic reduction process was also studied in range of 30 °C to 120 °C.

## **1.1 Problem Statement**

Nowadays, the concentration of CO<sub>2</sub> in atmosphere is getting higher. Due to the difficulties to reduce or treat CO<sub>2</sub> in environment, photo-catalytic reduction of CO<sub>2</sub> is the most promising method compared to conventional method to convert CO<sub>2</sub> to valuable products such as methanol.

Treating CO<sub>2</sub> is very important due to the long term effects to the environment. In conjunction to that purpose, photo-reduction process assisted with catalyst is the best method to be considered to treat CO<sub>2</sub> due to the process will converting CO<sub>2</sub> to methanol or methane without produces more poisonous gaseous.

## **1.2 Research Objectives**

The objectives of this study are:

- To study the best solvents in photo-catalytic reduction of CO<sub>2</sub>.
- To study the effect of temperature on photo-catalytic reduction process.

## **1.3 Scopes of Study**

Titanium dioxide, (TiO<sub>2</sub>) was selected as a catalyst in photo-reduction process due to its photo-stability, non-toxicity, redox efficiency and availability. Recently, it was shown that this self-organized TiO<sub>2</sub> exhibit very high photo-catalytic efficiency that can be used for the decomposition of organic compounds in the contact mode either in the Ti substrate or in flow-through UV irradiated membranes. The decomposition efficiency can be further enhanced by using a bias voltage or by coating TiO<sub>2</sub> with noble metal nanoparticles as stated by Kalbacova et. al., (2008).

According to Miyazaki and Iacono, (n.d) said that various chemical species especially ions, are known to be absorbed onto alumina. Thus, alumina is a typical support for the catalyst. In photo-reduction process, they are a lot of metal supported catalysts are prepared using alumina as their support. Therefore, in this study  $\text{Al}_2\text{O}_3/\text{TiO}_2$  as heterogeneous catalyst was used in photo - reduction process to convert waste to useful product.

#### **1.4 Organization of the Thesis**

This thesis consists of five chapters. In chapter one which is introduction was generally to identify all related elements for this study. The topic discussed in this chapter was introduction to  $\text{CO}_2$ ,  $\text{Al}_2\text{O}_3\text{-TiO}_2$  as a catalyst and methanol as a main product. The objectives and the scope of the experiment were also stated in this chapter.

Chapter two is the Literature Review where all elements stated in Chapter one were elaborated in more details. At the beginning of this chapter, the introduction to  $\text{CO}_2$  was spoken in large aspects where the causes, processes, advantages and disadvantages of  $\text{CO}_2$  were revealed. Next part is photo-reduction process of  $\text{CO}_2$ . In photo-reduction process, there were several elements were discussed. They were catalysts, solvents and temperatures. Then, the last part was discussed about methanol as a main product. In this part, the introduction to methanol was exposed in more specific where the concentrations of methanol and usage and alternatives route for methanol production were discussed.

The processes to obtain methanol was described on chapter three which labelled as methodology. In this part, all the steps from the very early to the end were clearly described. First step was the preparation of catalysts via sol-gel method. Then, the photo-reduction process was done regarding to the both parameters which were effects of solvents and reaction temperatures. The last part was analysis by using high performance liquid chromatography (HPLC). In this part, the procedures to obtain methanol were extended to the chapter four.

Chapter four is the part for results and discussion. In this part, the graphs were plotted to identify the highest concentration of methanol for every parameters. Then, the variation of the results were also discussed where the problem and weakness of the method used was defined.

Finally, chapter five is the part to conclude the experiment according to the result obtained. In this part also, several suggestions were inspired to deliver better result for the future.

## **CHAPTER TWO**

### **LITERATURE REVIEW**

#### **2.0 Introduction to Carbon Dioxide (CO<sub>2</sub>)**

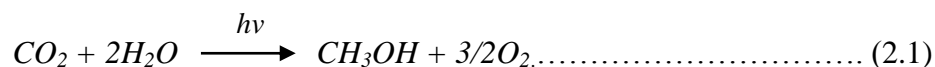
Asian Global Atmosphere Watch (GAW) Greenhouse Gases Newsletter, (2010) was reported that greenhouse gases such as carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) and chlorofluorocarbons (CFCs) are the primary causes of global warming. Among them, CO<sub>2</sub> is released mainly by the burning of fossil fuels. Over the past decades, the atmospheric concentration of CO<sub>2</sub> has been increasing owing to the expanded human activity, which consequently has accelerated the greenhouse effect. On the other hand, the consumption of fossil fuels worldwide gradually increases year after year because of the strong demand for human activities. Therefore, converting CO<sub>2</sub> to valuable hydrocarbons is one of the best solutions to both the global warming and the energy shortage problems (Hussain et. al., 2003).

In nature,  $\text{CO}_2$  is removed from the environment by photosynthesis. The energy obtained from sunlight is ultimately used to convert  $\text{CO}_2$  into glucose or a sugar molecule that stores sun energy in the form of chemical energy. Except geothermal or nuclear energy, most energy forms, such as fossil fuel, bio-material, hydropower and wind are simply transformations of sun energy either in the past or present. Thus, solar energy is the Earth's ultimate energy supply. One of the promising routes is that artificial photosynthesis may be implemented via the photo-reduction of  $\text{CO}_2$  to produce hydrocarbons. Therefore, solar energy is directly transformed and stored as chemical energy.

Jeffrey (2009) was stated that photo-catalytic reduction of  $\text{CO}_2$  whose transform to chemicals such as methane or methanol is particularly interesting and achieving a high efficiency for this reaction and extremely desired. Methanol can be easily transported, stored and used as gasoline-additives for automobiles. Moreover, methanol can be transformed into other useful chemicals using conventional chemical technologies.

## **2.1 Photo-Reduction of $\text{CO}_2$**

The energy grade of  $\text{CO}_2$  is low from a thermodynamic perspective, which is why any transformation to hydrocarbon requires energy infusion. **Eq. (2.1)** gives an example of the overall photo-reduction of  $\text{CO}_2$  to methanol as stated by Jeffrey (2009).



Based on thermodynamics as stated by Jeffrey (2009), converting one mole of CO<sub>2</sub> into methanol requires 228 kJ of energy at 298 K. Furthermore, the Gibbs free energy of **Eq. (2.1)** is 698.7 kJ at 298 K indicating that the equilibrium is highly unfavorable to the product, methanol and oxygen. The energy source should be provided without producing more CO<sub>2</sub>.

Photo-catalytic reduction is defined as "acceleration by the presence of a catalyst". A catalyst does not change in itself or being consumed in the chemical reaction. This definition includes photosensitization, a process by which a photochemical alteration occurs in one molecular entity as a result of initial absorption of radiation by another molecular entity called the photosensitized (Marta et. al., 2011).

## 2.2 Efficiency of CO<sub>2</sub>

Nature captures and recycles atmospheric CO<sub>2</sub> efficiently in its photosynthetic cycle. To chemically recycle CO<sub>2</sub> to methanol, it is necessary to be able to capture it from industrial or natural sources conveniently and economically in a pure form. This is currently best achieved by capturing and recycling CO<sub>2</sub> from sources where it is present in a sufficiently high concentration, through physical-chemical absorption and



desorption cycles coupled when needed with chemical purification particularly from  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  and other accompanying pollutants (George et. al., 2008).

### **2.3 Significance of $\text{CO}_2$ recycling for methanol production**

The recycling of  $\text{CO}_2$  from industrial or natural emissions and capture of  $\text{CO}_2$  from the atmosphere provides a renewable, inexhaustible carbon source and could also allow the continued use of derived carbon fuels in an environmentally carbon neutral way. As discussed presently, the captured  $\text{CO}_2$  would be stored/sequestered in depleted gas and gas and oil- fields, deep aquifers, underground cavities, at the bottom of the seas, etc. This, however, does not provide a permanent safe solution, nor does it help our future needs for fuels, hydrocarbons, and their products (George et.al., 2008).

Recycling of the  $\text{CO}_2$  via its chemical reduction with hydrogen to produce methanol offers in contrast a viable new permanent alternative. As fossil fuels are becoming scarcer, capture and recycling of  $\text{CO}_2$  and eventually atmospheric  $\text{CO}_2$  would continue to support production and use of carbon-containing fuels such as methanol, DME, and all the synthetic hydrocarbons and their needed products. We do not believe that humankind is facing an energy crisis. We are, after all in the final analysis, obtaining most of our energy in one form or another from the sun. Using this approach, there will be no need to change drastically the nature of our energy use, storage, and transportation infrastructure or the continued use of synthetic hydrocarbons and products. As  $\text{CO}_2$  is available to everybody on Earth, it would liberate us from the

reliance on diminishing and nonrenewable fossil fuels frequently present only in geopolitically unstable areas (George et. al., 2008).

## **2.4 Introduction to Catalyst**

Catalyst can be defined as a substance that causes or accelerates a chemical reaction without itself being affected. Catalyst usually used in small amounts relative to the reactants that modifies and increases the rate of a reaction without being consumed in the process (Ricardo et. al., 2006).

### **2.4.1 Alumina ( $\text{Al}_2\text{O}_3$ )**

$\text{Al}_2\text{O}_3$  catalysts are widely used in different industrial chemical processes such as hydrodesulphurization, dehydration, cracking and others. Most of the  $\text{Al}_2\text{O}_3$  produced commercially is obtained by the calcinations of aluminum hydroxide which also frequently termed alumina tri-hydrate or ATH. The aluminum hydroxide is virtually all made by the Bayer Process. This involves the digestion of bauxite in caustic soda and the subsequent precipitation of aluminum hydroxide by the addition of fine seed crystals of aluminum hydroxide (Gaurav et. al., 2010).

As transition alumina has higher surface area and chemical activity, it has been used extensively as a catalyst or catalyst support because of the excellent properties such as high surface area, good catalytic activity, good mechanical strength, high hardness and transparency. But, when it is used at higher temperature such as the catalytic combustion of hydrocarbons and catalytic purification for the exhaust of vehicle, the superiority of alumina will lose in both structural grounds (transformation of active alumina to corundum) and textural grounds (loss of surface area and porosity). It is the reason that increasing physical properties and thermal stability of transition alumina is of primary industrial interest (Xiaohong et. al., 2005).

Generally, the stabilization of alumina can be promoted by doping it with foreign elements such as alkaline-earth metals, rare-earth metals and silicon, and by improving the synthesis method or by a combination of two means above (Xiaohong et. al., 2005).

#### **2.4.2 Titanium Dioxide (TiO<sub>2</sub>)**

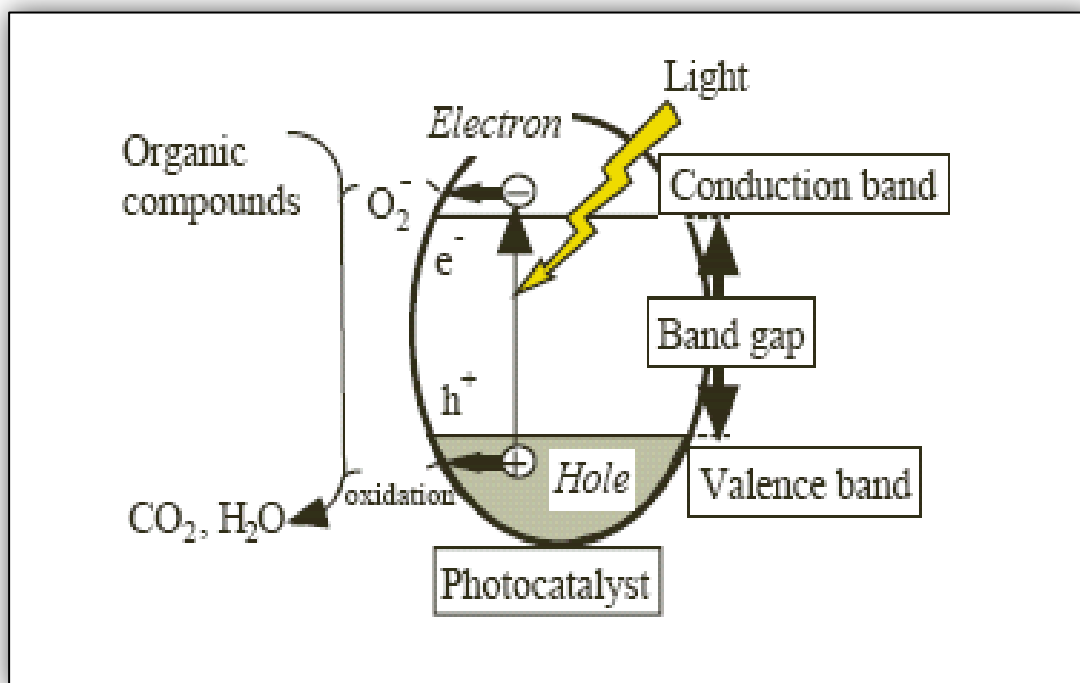
TiO<sub>2</sub> is a fine white powder. It is more effectively than any other white pigment. Therefore, TiO<sub>2</sub> are highly used to whitening product. TiO<sub>2</sub> is one of the most applied and important material used by the paints and plastics industry for whiteness and opacity (Chor et. al., 1992).

TiO<sub>2</sub> particularly in the anatase form, is a photo-catalyst under ultraviolet (UV) light. Recently, it has been found that TiO<sub>2</sub>, when spiked with nitrogen ions or doped with metal oxide like tungsten trioxide, is also a photo-catalyst under either visible or UV light. The strong oxidative potential of the positive holes oxidizes water to create hydroxyl radicals. It can also oxidize oxygen or organic materials directly. TiO<sub>2</sub> is thus added to paints, cements, windows, tiles, or other products for its sterilizing, deodorizing and anti-fouling properties and is used as a hydrolysis catalyst. It is also used in dye-sensitized solar cells, which are a type of chemical solar cell (Ana-Lilia and Juan-Carlos, 2008).

The photo-catalytic properties of TiO<sub>2</sub> were discovered by Akira Fujishima in 1967 and published in 1972. The process on the surface of TiO<sub>2</sub> was called the Honda-Fujishima effect. TiO<sub>2</sub> has potential for use in energy production. As a photo-catalyst, it can carry out hydrolysis where it can break water into hydrogen and oxygen. As the hydrogen collected, it could be used as a fuel. The efficiency of this process can be greatly improved by doping the oxide with carbon. Further efficiency and durability has been obtained by introducing disorder to the lattice structure of the surface layer of TiO<sub>2</sub> nano-crystals, permitting infrared absorption (Afendi and Mutalib, 2009).

### 2.4.3 Mechanism of titanium dioxide (TiO<sub>2</sub>)

When photo-catalyst TiO<sub>2</sub> absorbs ultraviolet (UV) radiation from sunlight or illuminated light source (fluorescent lamps), it will produce pairs of electrons and holes. The electron of the valence band of TiO<sub>2</sub> becomes excited when illuminated by light and the mechanism of photo-catalysis is shown in **Fig. 2.1**. The excess energy of this excited electron promoted the electron to the conduction band of TiO<sub>2</sub>, therefore creating the



**Fig. 2.1:** Mechanism of Photo-reduction (MCH Nano Solution, n.d.)

negative electron (e<sup>-</sup>) and positive hole (h<sup>+</sup>) pair. This stage is referred as the semiconductor's 'photo-excitation' state. The energy difference between the valence band and the conduction band is known as the 'Band Gap'. Wavelength of the light necessary for photo-excitation is 388 nm (Nano Protection, n.d.).

The positive-hole of  $\text{TiO}_2$  breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative electron reacts with oxygen molecule to form super oxide anion. This cycle continues when light is available (kathirvelu et. al., 2008).

## **2.5 Effect of Solvents**

In this experiment, solvent was used in order to complete one reaction cycle. As the appearance of solvent is justified, it will change the production quality. The ratio of products was greatly influenced by the kind of solvent and increased dielectric constant of the solvent. Solvent is very important for the production purpose. It can determine what the product formed. For example, if propylene carbonate was used as the solvent, methanol is produced with the bulk  $\text{TiO}_2$  photocatalyst. Meanwhile, photo-catalytic reduction of  $\text{CO}_2$  on the alumina doped  $\text{TiO}_2$  film in acetonitrile in the presence of 2-propanol was resulted in the formation of formate and carbon monoxide as the reduction products (Liu et. al., 1997).

Another effect of solvent is polarity. As for photochemical reduction process, the selectivity of the formation of CO and/or  $\text{HCOOH}$  is determined by the adsorption strength of CO. If a metal electrode, such as a transition metal, that allows strong adsorption of CO is used, the negative charge of the oxygen atom of CO will increased as a result of back-donation from an occupied metal orbital to an unoccupied  $\text{CO}_2$

orbital. Then, protonation is promoted to break the oxygen atom from the anion radical to yield carbon monoxide as the reduction product. When low polar solvents such as  $\text{CCl}_4$  and  $\text{CH}_2\text{Cl}_2$  are used, the  $\text{CO}^-$  with anion radicals formed may be adsorbed strongly on Ti sites of the  $\text{TiO}_2$  because the anion radicals are not highly solvated in solvents of low polarity (Liu et. al., 1997).

The negative charge of one oxygen atom of  $\text{CO}^-$  is increased as mentioned above. Carbon monoxide formation occurs readily with removal of the oxygen atom of the  $\text{CO}^-$  anion radical by a proton. If solvents of high dielectric constant such as water and propylene carbonate are used, the  $\text{CO}^-$  anion radicals formed may be greatly stabilized by the solvents resulting in weak interaction with the photo-catalyst surface. Then the carbon atom of the  $\text{CO}^-$  anion radical tends to react with a proton to give formate. It is concluded that the polarity of solvents used in the photo-reduction of  $\text{CO}_2$  plays the most crucial role in determining the kind of reduction products either CO or formate (Liu et. al., 1997).

### **2.5.1 Water as Solvent**

Water is a good solvent due to its polarity. The solvent properties of water are vital in biology, because many biochemical reactions take place only within aqueous solutions. When an ionic or polar compound enters water, it is surrounded by water molecules. The relatively small size of water molecules typically allows many water molecules to surround one molecule of solute. The partially negative dipoles of the

water are attracted to positively charged components of the solute, and vice versa for the positive dipoles (Giakos, 2006).

According to Ikeue et. al., (n.d), in photo-catalytic reduction of  $\text{CO}_2$  using Ti- $\beta$  zeolite catalyst, the final products were  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$ . They conclude that water molecules can more easily gain access to the tetrahedral coordinated titanium oxide species, Ti- $\beta(\text{OH})$ , but high selectivity for the formation of  $\text{CH}_3\text{OH}$  was observed on Ti-  $\beta(\text{F})$ . Meanwhile, higher copper dispersion and smaller copper particles on the titania surface correspond to a greater improvement in  $\text{CO}_2$  photo-reduction performance by using sol-gel prepared  $\text{Cu/TiO}_2$  as the catalyst and water as the solvent (Tseng et. al., n.d).

### **2.5.2 Sodium Hydroxide (NaOH) as Solvent**

As stated by Tseng et. al., (n.d), photo-catalytic reduction of  $\text{CO}_2$  by using NaOH as solvent can lead to the production of methanol by the presence of  $\text{Cu/TiO}_2$  as catalyst and emitted by 254 nm of UV light. They stated that higher copper dispersion and smaller copper particles on the titania surface correspond to a greater improvement in  $\text{CO}_2$  photo-reduction performance as well as selectivity of methanol as major product when NaOH is applied as solvent for photo-reduction of  $\text{CO}_2$  process.

NaOH solution was crucial in the photo-reduction of  $\text{CO}_2$ . The concentration of methanol substantially increased with the addition of NaOH in our experiments, perhaps due to the following two reasons. First, the high concentration of  $\text{OH}^-$  where ions in